Report on the outcomes of a Short-Term Scientific Mission[1]

Action number: CA21126 (NanoSpace)

Grantee name: Jacob Allitt

Details of the STSM

Title: Space-abundant Transition Metal Astrocatalysis: A quantum mechanical approach

Start and end date: 13/06/2024 to 21/06/2024

Description of the work carried out during the STSM

Description of the activities carried out during the STSM. Any deviations from the initial working plan shall also be described in this section.

(max. 500 words)

The activities carried out during the STSM were conducted according to the workplan, with the primary goal of supporting independent quantum chemical calculations on silica supported Fe single atom (SA) and nanocluster (NC) systems to complement future experiments performed at HWU. After an introduction to the quantum grain group of Prof. Rimola, Dr Gerard Pareras, an expert in CP2K, provided an insight into the capabilities of CP2K for supporting calculations. I was also introduced to other members of the group, who helped create the silica structures through molecular dynamics simulations. To create the SA system, a single Fe atom was added to the surface before relaxing the geometry using CP2K to obtain a structure suitable as a basis for future calculations. For the NC, a cluster of 13 Fe atoms was introduced and allowed to relax across the silica grain surface.

In getting familiar with the code, it was detailed how to adjust input parameters to deliver specific types of calculations (Geometry Optimisation, NEB-TS, Vibrational Analysis); specifying basis sets, functionals, charge and multiplicity, as well as adjusting convergence criteria, maximum number of SCF iterations and subsystem cell parameters, just to name a few. In addition to input parameters, I was shown what data is generated in specific output files, how to process resulting data as well as how to identify any issues. Furthermore, I was also shown additional capabilities of CP2K in generating visualisation of molecular orbitals, as well as how to simulate X-Ray spectroscopies. The latter of which will be of significant use in the future to compare with experimentally obtained spectra.

[1] This report is submitted by the grantee to the Action MC for approval and for claiming payment of the awarded grant. The Grant Awarding Coordinator coordinates the evaluation of this report on behalf of the Action MC and instructs the GH for payment of the Grant.

Moving onwards, in further developing the previous work of Fischer-Tropsch (FT) methanol synthesis, the group was exploring ethanol synthesis by means of a chain growth mechanism, initiated through CO dissociation of acetaldehyde forming CH2 [1]. In accordance with the work plan and contrary to the work of Prof. Rimola's group in aiming to form ethanol, CH2 was used instead as a starting point to create a reaction network aiming towards polymerisation, aromatisation, and cyclisation, through successive addition of CH2, C2H2, C2H4 and other astronomically significant molecules to the Fe SA and NC systems. All the above substituents have been identified in interstellar environments [2] and were natural starting points as all are potential products of the FT reaction. As we continue to build this reaction network, we hope to identify key intermediate species, in the formation of larger chain and cyclic products.

Description of the STSM main achievements and planned follow-up activities

Description and assessment of whether the STSM achieved its planned goals and expected outcomes, including specific contribution to Action objective and deliverables, or publications resulting from the STSM. Agreed plans for future follow-up collaborations shall also be described in this section.

(max. 500 words)

Whilst this STSM has been incredibly insightful and certainly achieved its primary objective in supporting independent submission and analysis of quantum chemical calculations by means of CP2K - as raised in the working plan, its overall measure of success will far extend this initial visit. Thanks to in-depth conversations with expert theoreticians, I feel confident in exploiting CP2Ks functionality in performing a range of calculations to both compliment and guide my future experiments at Heriot-Watt.

As with most computational chemistry, the limiting factor during my time at UAB has been time. Whilst calculations continue, thus far the main achievements resulting on the Post FT work are as follows:

- Started to develop a CH_2 addition reaction pathway (Figure 1) built up of "reactants" and "products", geometrically optimised with the semi-local PBEsol functional and Grimme D3(BJ) dispersion correction. Here, the Gaussian double- basis set DZVP-MOLOPT-SR-GTH was used for all atom types.
- Started the process of computing transition state structures employing the climbing-image nudged elastic band method (NEB-CI) as implemented in CP2K.
- Began computing harmonic frequencies through vibrational analysis calculations to both validate transition state structures and correct the ZPE.
- Used resulting energies to formulate preliminary energy profile diagrams to determine feasibility and stability of molecular formation.

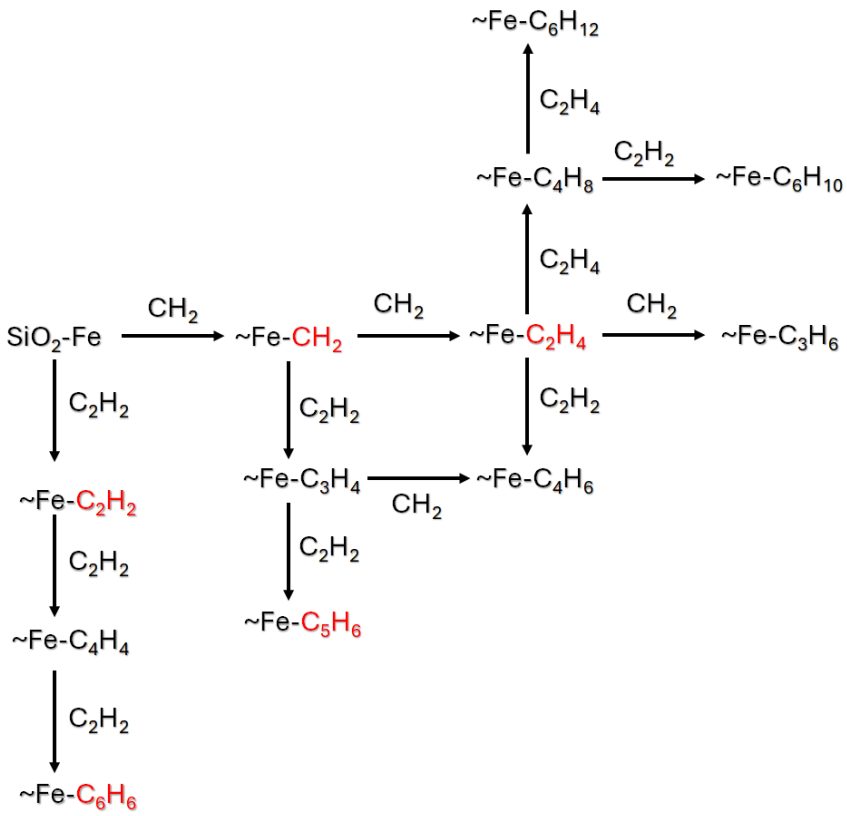


FIGURE 1 – Reaction Pathway investigated thus far, through geometry optimisations of “reactants” and “products”. NEB-TS calculations ongoing and expansion of network to continue. Red: Molecules detected in ISM [1].

Whilst some discussion was had into using the data to compute binding energies, the computational time did not permit us to do so at this stage. However, these calculations will continue as I return to Heriot-Watt, continuing to develop the reaction network and create a story for the formation of interstellar complex organic molecules towards polycyclic aromatics and eventually nanocarbons. This work represents a key step in supporting my studies and as such, we begin the work towards catalytic formation of nanocarbons. Once the data is more complete, discussions will continue towards computing binding, desorption, and activation energies, with another visit to the quantum grain group to accompany further calculations hopeful. Furthermore, in mechanisms producing products of excess hydrogen for aromaticity, dehydrogenation reactions will be explored.

Finally, I have also used this time to expand my personal network, creating opportunities for dialogue with other PhD students, post-docs and academics who can also provide great insight in any future experimental or computational projects.

I thank the COST action CA21126 Nanospace for providing this opportunity and to Universitat Autònoma de Barcelona for hosting me.

[1] Pareras, G. et al. (2024) ‘Single-atom catalysis in Space II. ketene--acetaldehyde--ethanol and methane synthesis via Fischer-Tropsch chain growth’, Astronomy & Astrophysics [Preprint]. doi:10.1051/0004-6361/202449378.

[2] McGuire, B.A. (2022) ‘2021 census of Interstellar, Circumstellar, extragalactic, protoplanetary disk, and exoplanetary molecules’, The Astrophysical Journal Supplement Series, 259(2), p. 30. doi:10.3847/1538-4365/ac2a48.